

## Toughening studies on an ABS/PC blend-modified epoxy resin system

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**Abstract.** Studies were carried out on the toughening of a bifunctional epoxy (diglycidyl ether of bisphenol-A) matrix system with an ABS/PC thermoplastic blend. The thermoplastic blend was incorporated into the epoxy matrix by particle dispersion and melt-mix methods. The unmodified and modified epoxy resin systems were cured with a stoichiometric quantity of diamino diphenyl methane (DDM). The cured castings were characterized by measurement of glass transition temperature ( $T_g$ ) by DSC, evaluation of plane strain fracture toughness ( $K_{IC}$ ) by three-point bending tests and SEM analysis of non-etched and base/acid etched fracture surfaces. In general ABS/PC-modified (15% w/w) epoxy-resin-cured systems showed enhanced fracture toughness without lowering the glass transition temperature. The melt-mix method yielded higher fracture toughness than the particle dispersion method; this conclusion was also supported by scanning electron micrographs.

### 1. Introduction

Of the thermosetting polymers, epoxy resins are one of the best matrix resin systems used for composite materials [1] of interest to aerospace engineers. Cured unmodified epoxy resins are brittle with inadequate fracture toughness [2–8], which limits their use in composites for high-performance applications. Several workers have reported that elastomer-modified epoxy resin systems showed enhanced fracture toughness [4–6, 9]. Later it was demonstrated that the incorporation of a thermoplastic phase to the brittle matrix enhances the fracture toughness [10]. In this context several studies have been reported on thermoplastic-modified epoxy resin systems [8, 9, 11–18]. Thermoplastic-toughened thermoset systems combine the toughness characteristics of the thermoplastic modifier with the processing advantages of a thermoset matrix system [19]. Thermoplastic-toughened epoxy resin systems exhibit enhanced fracture toughness [8, 10, 12, 16]. Toughening of epoxy with bisphenol-A polycarbonate [11] gave improved fracture toughness, while toughening of epoxy with polycarbonate and rubber (ETBN) gave no improvement in fracture toughness [20].

With this background it is of great interest to explore the toughenability of a bifunctional epoxy resin modified with a quaternary polymer blend containing

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acrylonitrile–butadiene–styrene (ABS) terpolymer and bisphenol-A polycarbonate (PC). The toughening process was carried out using two approaches, namely a particle dispersion technique and a melt-mixing technique. The glass transition temperature ( $T_g$ ) and plane strain fracture roughness ( $K_{IC}$ ) of unmodified and modified resin systems were evaluated and are reported in this paper.

## 2. Experimental details

### 2.1. Materials

The epoxy resin used in the studies was diglycidyl ether of bisphenol-A (DGEBA coded LY-556) and the curing agent used was 4,4'-diamino diphenyl methane (DDM coded HT-972). Both were obtained from Ciba Geigy (India) Ltd. ABS/PC blend (55:45 w/w in granular form) was supplied by Bhansali Engineering Polymers Ltd (India).

### 2.2. Blending and curing of the particle-dispersed-modified epoxy resin system

ABS/PC particles were prepared by dissolving ABS/PC granules in tetrahydrofuran (THF) followed by reprecipitation with methanol. The precipitated particles were filtered and dried at 80 °C for 1 h. The formulation used was epoxy/ABS/PC particles/DDM = 100/15/27 (w/w). DDM in the fused state at 120 °C was mixed with preheated epoxy (80 °C) and then the ABS/PC particles were dispersed. The hot mixture was then poured into a preheated (80 °C) aluminium mould and heated to 150 °C for 3 h in an air oven. Finally the oven was turned off and the cured castings were allowed to cool slowly to room temperature.

### 2.3. Blending and curing of the melt-mixed epoxy resin system

Blending of ABS/PC in epoxy was carried out by using the formulation epoxy/ABS-PC granules/DDM = 100/15/27 (w/w). The epoxy resin was heated to about 160 °C and the ABS/PC granules (dried at 80 °C for 1 h) were added and stirred continuously for 30 min at 160 °C until they were thoroughly mixed into the epoxy matrix. The mix was cooled to about 80 °C, then the molten DDM was added and stirred. The resulting mixture was poured into a preheated aluminium mould and cured at 150 °C for 3 h; the cured castings were cooled to room temperature as mentioned in section 2.2.

### 2.4. Material characterization

The glass transition temperature ( $T_g$ ) of the cured plaques was determined by using a differential scanning calorimeter (DSC-2910-TA Instruments) over a temperature range of 22 °C to 250 °C. All the samples were heated up to 250 °C twice inside the calorimeter. The thermograms obtained clearly confirmed complete curing of the resin systems.

Plane strain fracture toughness ( $K_{IC}$ ) values were evaluated as per the ASTM-E-399-74 test method using three-point bending specimens having a geometry as shown in figure 1.

The central 'U' notch of 3 mm depth on one edge of the specimen was machined and then a sharp notch of 0.2 mm depth was introduced by pressing a razor blade into the tip of the U notch. The specimens were loaded in three-point bending configuration with a span length of 40 mm in a universal testing machine (INSTRON model 6025).

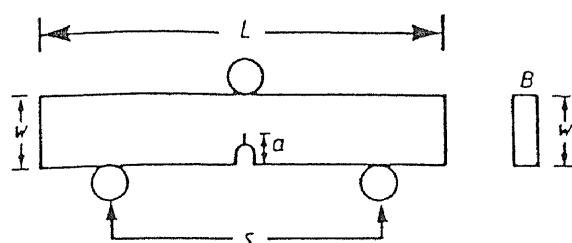


Figure 1. Three-point bending specimen configuration for plane strain fracture toughness evaluation as per ASTM-E399-74 (see [8]). Specimen dimensions: length,  $L = 64$  mm; width,  $W = 10$  mm; thickness,  $B = 3$  mm; span length,  $s = 40$  mm; crack length,  $a = 3.2$  mm.

$$K_{IC} = \frac{PS}{BW^{3/2}} f(a/w)$$

where  $f(a/w) = 1.61$ .

Table 1. Fracture toughness ( $K_{IC}$ ) values.

Resin system	$K_{IC}$ (MPa m <sup>1/2</sup> )
Unmodified epoxy-DDM	34.53
ABS/PC particle-dispersed epoxy-DDM	54.37
ABS/PC melt-mixed epoxy-DDM	70.84

at a cross head speed of  $1 \text{ mm min}^{-1}$  at  $22^\circ\text{C}$  and 55% relative humidity. Six specimens were tested in each case and the average  $K_{IC}$  values obtained are reported in table 1.

A few of the fractured specimens were etched as in the report by Dong *et al* [21]. The etched and non-etched fractured surfaces were then examined in a scanning electron microscope (SEM; Joel-JSM-840A) to obtain the micrographs as shown in figures 3–11.

### 3. Results and discussions

#### 3.1. Glass transition temperature ( $T_g$ )

DSC thermograms (figure 2) showed that the unmodified and modified resin systems exhibit similar  $T_g$  values. This may be mainly due to the almost identical  $T_g$  values of the ABS/PC modifier ( $154^\circ\text{C}$ ) and the resin system ( $158^\circ\text{C}$ ).

#### 3.2. Fracture toughness

Fracture toughness values ( $K_{IC}$ ) presented in table 1 indicate that the ABS/PC particle-dispersed resin system shows enhancement in  $K_{IC}$  values of 1.5 times that of the unmodified resin system. This is due to the process of energy absorption by dispersed ABS/PC particles in the matrix. This is further clearly evidenced in the SEM micrographs (see figures 6 and 7). The ABS/PC melt-mixed resin system exhibits enhancement in  $K_{IC}$  values twice that of the unmodified resin system. This is due to higher energy absorption by plastic deformations in the matrix as supported by SEM studies (see figures 8 and 9).

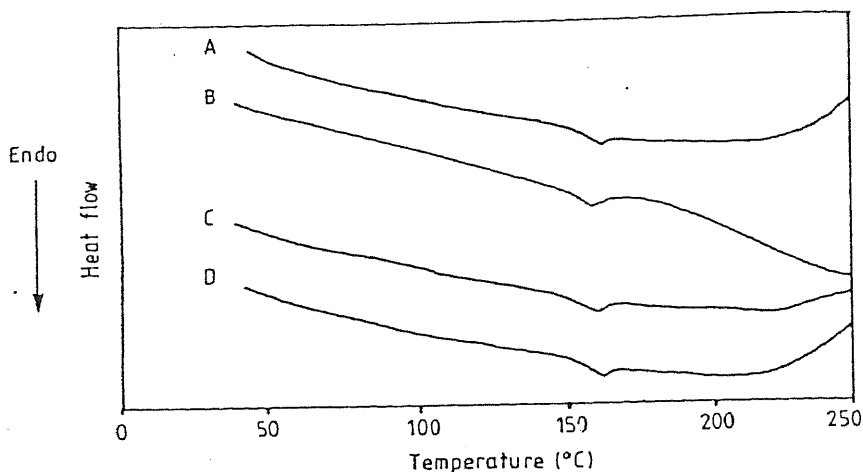


Figure 2. DSC thermograms of cured resin systems: A, unmodified epoxy-DDM; B, ABS/PC particles; C, ABS/PC particle-dispersed epoxy-DDM; D, ABS/PC melt-mixed epoxy-DDM.

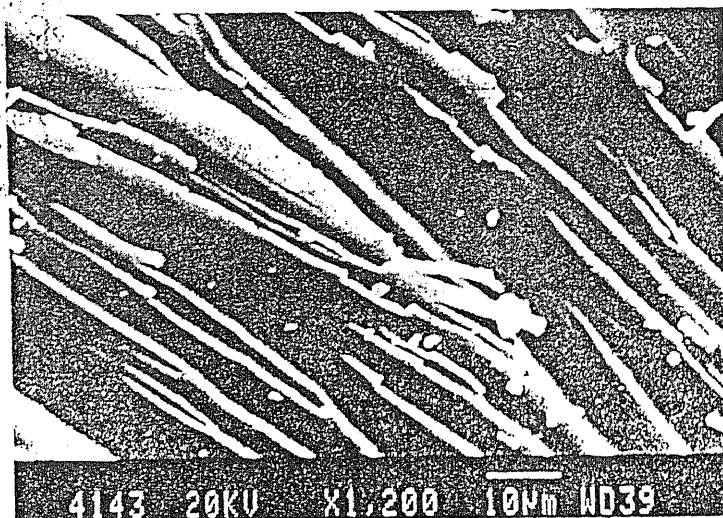


Figure 3. SEM micrograph of fractured surface of epoxy-DDM casting.

### 3.3. Fractographic analysis

Scanning electron micrographs (figures 3 and 4) reveal the fractured-phase morphology of unmodified epoxy resin-DDM and ABS/PC modifier. An uninterrupted crack propagation pattern near the notch tip of the fractured unmodified epoxy-DDM system is clearly seen in figure 5. Figure 6 shows crack propagation near the notch tip for the ABS/PC particle-dispersed resin system. The features clearly show that the crack propagation is delayed by ABS/PC domains. Further, figure 7 exhibits crack inhibition by agglomerated ABS/PC particles [22]. These two micrographs (figures 6 and 7) amply represent the contribution of ABS/PC particles to the containment of the crack growth.

Figure 8, an SEM of the ABS/PC melt-mixed resin system, shows that crack propagation near the notch tip is delayed by plastic deformation exhibited by the matrix. A close-up of this plastic deformation process can be visualized clearly in figure 9. The higher energy absorption by the melt-mixed resin system is obviously due to the yielding behaviour of the matrix.

Etched fracture surfaces of the ABS/PC particle-dispersed system (figures 10 and

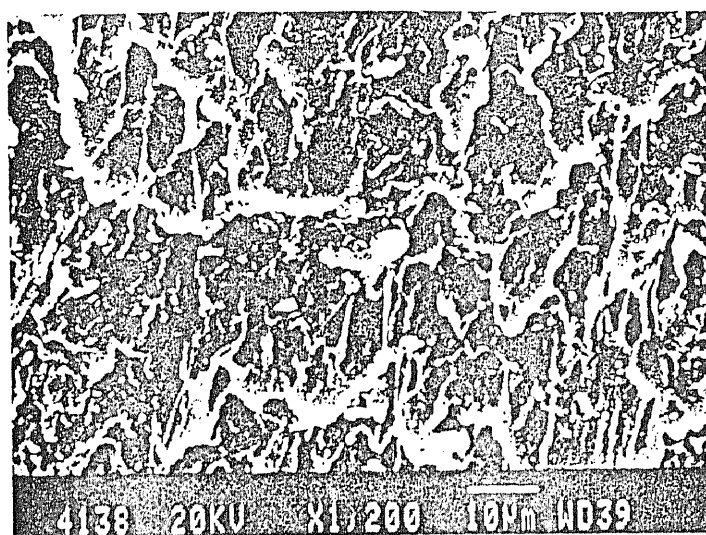


Figure 4. SEM micrograph of fractured surface of ABS/PC granules.



Figure 5. SEM micrograph of fractured surface of epoxy-DDM casting. (Crack propagation pattern near notch tip.)

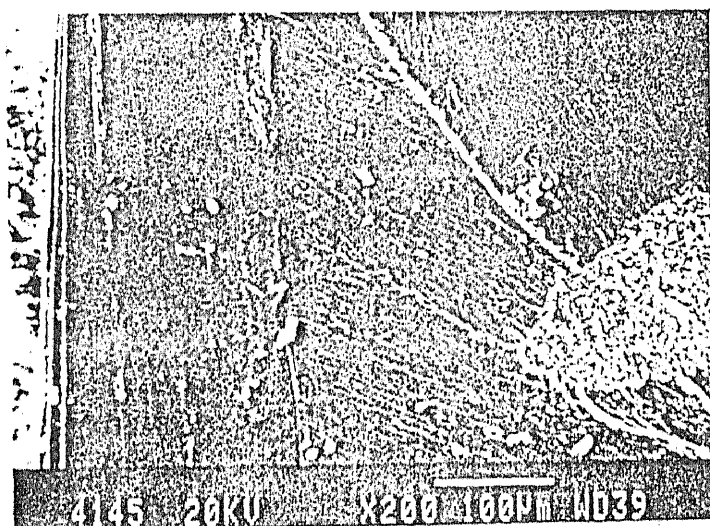


Figure 6. SEM micrograph of fractured surface of ABS/PC particle-dispersed epoxy-DDM casting. (Crack propagation pattern near notch tip.)

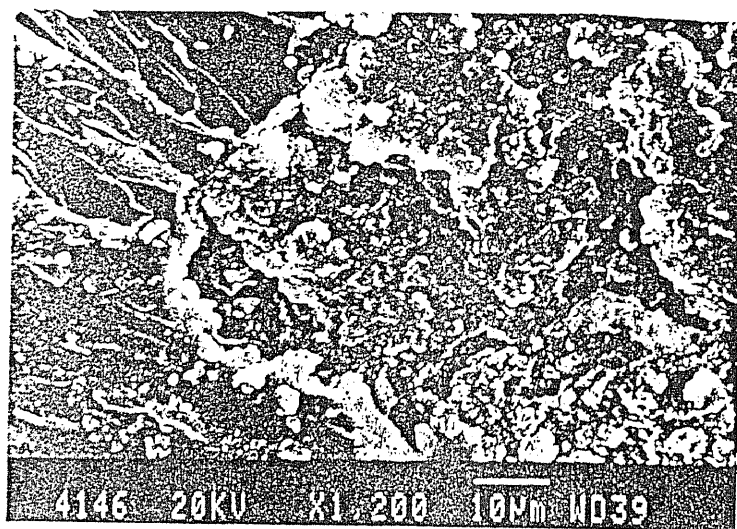


Figure 7. SEM micrograph of fractured surface of ABS/PC particle-dispersed epoxy-DDM casting. (Closer view (higher magnification) of the interface between ABS/PC particles and resin matrix.)

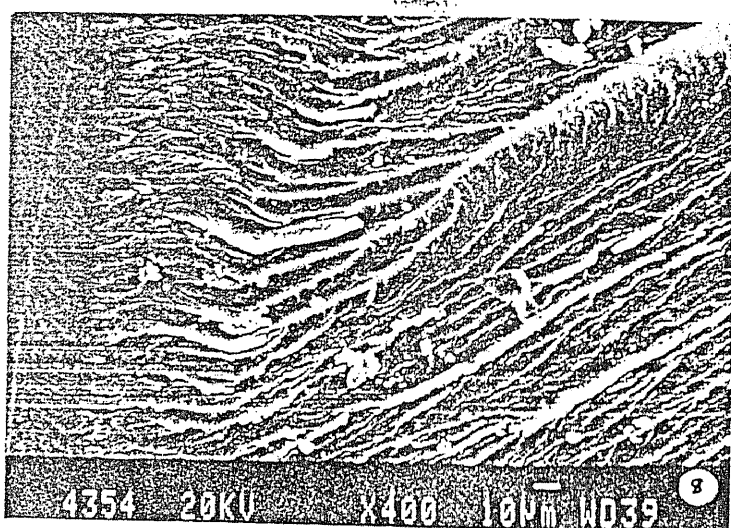


Figure 8. SEM micrograph of fractured surface of ABS/PC melt-mixed epoxy-DDM casting. (Crack propagation near notch tip.)

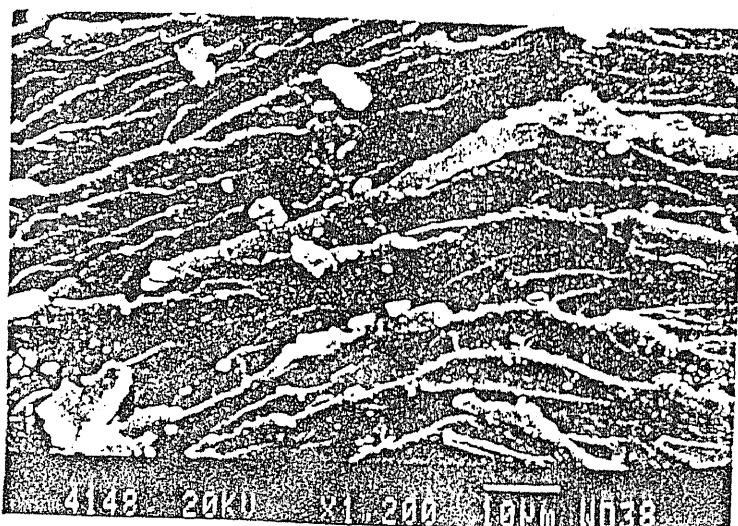


Figure 9. SEM micrograph of fractured surface of ABS/PC melt-mixed epoxy-DDM casting. (Higher magnification.)



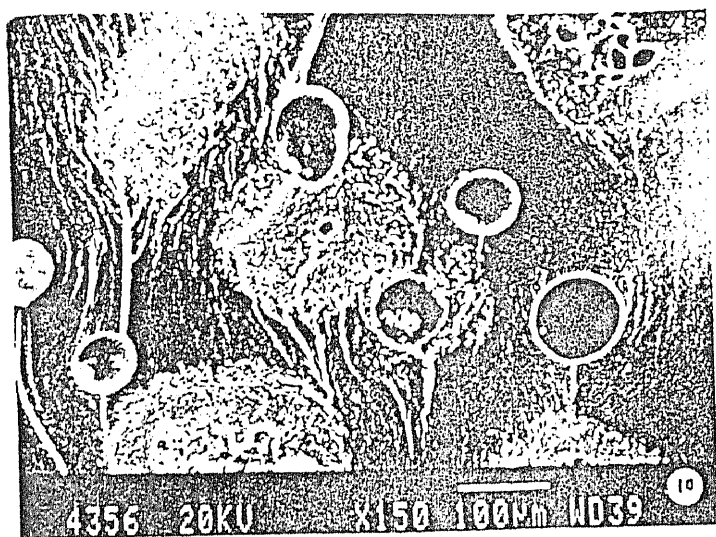


Figure 10. SEM micrograph of etched, fractured surface of ABS/PC particle-dispersed epoxy-DDM casting. (Lower magnification.)

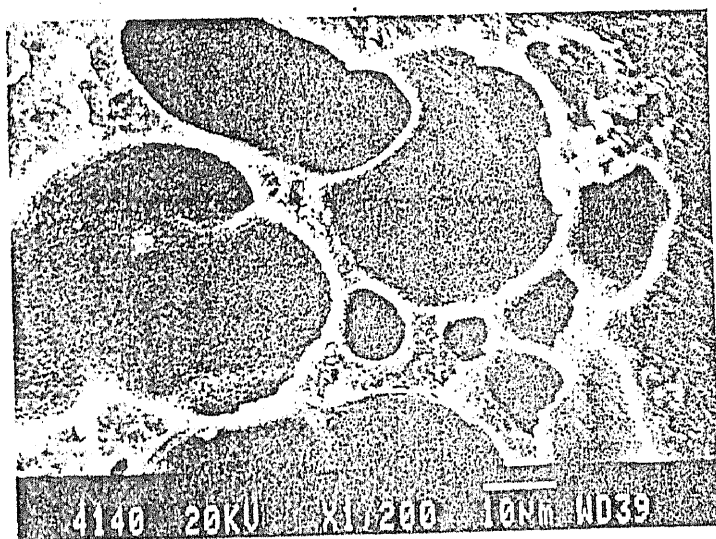


Figure 11. SEM micrograph of etched, fractured surface of ABS/PC particle-dispersed epoxy-DDM casting. (Higher magnification.)

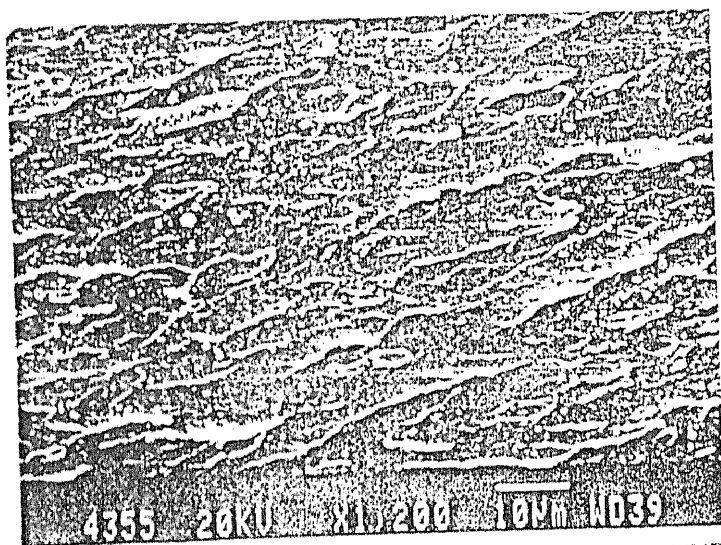


Figure 12. SEM micrograph of etched, fractured surface of ABS/PC melt-mixed epoxy-DDM casting.

11) exhibit several deep pits in the matrix, which are caused by the dissolution of ABS particles by base/acid etching. These micrographs also clearly indicate that the ABS particles are embedded in the resin matrix without any strong crosslinkages.

The etched fractured surface of the ABS/PC melt-mixed system (figure 12) exhibits no such deep pits in the matrix, which clearly reveals that the ABS/PC modifier is intimately mixed with the resin matrix phase.

#### 4. Conclusions

An ABS/PC thermoplastic blend was incorporated into a bifunctional DGEBA epoxy resin to the extent of 15% (w/w) by particle dispersion and melt-mix methods. A comparative evaluation was made of the two types of blended products both cured with a diamino diphenyl methane amine hardener under similar conditions. We can conclude that the ABS/PC thermoplastic blend in general enhanced the fracture toughness ( $K_{IC}$ ) of the epoxy-DDM matrix system without lowering  $T_g$  and that the ABS/PC melt-mix method yielded a higher fracture toughness than the particle dispersion method.

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